30 on Chromosorb). Normal column temperatures for arsine chromatographic analysis were 200–215° with inlet and detector blocks at least 50° higher.

The lithium diphenylarsenide was prepared in 0.1-mole quantities and diluted to 100-ml solutions in THF. Reactions employed aliquots of this quantity. Care was taken to dry all reagents before reaction. The THF was dried over calcium hydride and filtered before use.

Preparation of Phenyllithium-Free Lithium Diphenylarsenide (I).—Triphenylarsine (30.6 g, 0.1 mole) was dissolved in 70 ml of THF (calcium hydride dried) and placed in a flask under nitrogen. Lithium metal rod (1.4 g, 0.02 mole) was washed with ether, pounded flat, cut into small squares, and added to the stirred arsine solution. After a 5-min induction period, the solution turned deep red (transient greenish yellow). As the reaction proceeded, the color darkened and enough heat was generated to cause the THF to come to reflux. After 20 min, the reaction began to subside. The mixture was allowed to cool to ambient temperature and stirred for 2 hr. The dark blackish red solution was transferred, under nitrogen, to a dropping funnel and the excess lithium was left in the funnel as the red solution was added to a clean setup. Since lithium is less dense than the solution, the separation was easily accomplished. To this solution 9.2 g (0.1 mole) of *t*-butyl chloride, in 25 ml of THF, was added slowly. Cooling was required to keep the solution near room temperature. When the addition was complete and no further gas was evolved, the color lightened to a yellower red. This solution was then transferred to a clean dropping funnel, diluted to 100 ml, and used as the stock solution for all reactions. It should be used within 12 hr to obtain good yields.

Preparation of *cis*-β-Styryldiphenylarsine (II).—In a dry setup was placed 1.83 g (0.01 mole) of *cis*-β-bromostyrene in 20 ml of THF. Lithium diphenylarsenide solution was decolorized immediately upon contact with the halide and the reaction was very exothermic. Upon completion of the addition, the solution was allowed to cool and the THF was removed with a rotary evaporator. The resulting oil was shaken with weakly basic water (approximately 5% KOH). After several minutes the oil solidified and was filtered. The resulting *cis*-β-styryldiphenylarsine was recrystallized from ethanol, yield 2.1 g (63.2%), mp 91–92°.

Anal. Calcd for $C_{20}H_{17}As$: C, 72.28; H, 5.14; As, 22.58. Found: C, 72.02; H, 5.23; As, 22.75.

The proton nmr spectrum of a deuteriochloroform solution of the *cis*-β-styryldiphenylarsine showed a complex phenyl proton signal centered at τ 2.65 and one-half of an AB vinyl proton signal, a doublet, J = 12 cps, at τ 3.5.

Preparation of *trans*-β-Styryldiphenylarsine (III).—In a dry setup, lithium diphenylarsenide solution, 25 ml (0.025 mole), was added slowly to 4.3 g (0.025 mole) of *trans*-β-bromostyrene (Eastman, contains 10% of *cis* isomer) in 25 ml of THF. The reaction was very exothermic and the arsenide was immediately decolorized upon contact with the halide. When the addition was complete, the solution was allowed to cool, the solvent was stripped off, and the resulting oil was distilled under vacuum. A small amount of unreacted *trans*-β-bromostyrene was recovered as forerun. The product, *trans*-β-styryldiphenylarsine, was collected (bp 187–189° at 0.25 mm), yield 5.9 g (71.3%). The proton nmr spectrum of a deuteriochloroform solution of III showed a complex proton signal at τ 2.7.

Gas Chromatographic Analysis of *cis*- and *trans*-β-Styryldiphenylarsines.—The isolated *cis*- and *trans*-β-styryldiphenylarsines were found to pass unisomerized through a $^1/_8$ in. × 4 ft, 3% SE 30 column at 200° with retention times of 1–1.5 min. The difference in retention times between the two isomers was sufficient to allow their separation and positive identification. A reaction mixture of 0.9 g (0.005 mole) of *cis*-β-bromostyrene and 5 ml (0.005 mole) of lithium diphenylarsenide in 10 ml of THF was prepared in a septum-topped bottle by the use of syringes. A similar solution, employing commercial *trans*-β-bromostyrene instead of the *cis* isomer was also prepared. The *cis* mixture showed only a single peak (aside from a small peak identified as unreacted triphenylarsine) which had a retention time identical with that of the isolated *cis*-β-styryldiphenylarsine. The *trans* mixture showed two peaks (beside the triphenylarsine peak). The ratio of the shorter retention time peak (identical with the isolated *cis* isomer) to the longer retention time peak (identical with the isolated *trans* isomer) was found to be 1:10 by mechanical integration. The commercial *trans*-β-bromostyrene was shown to contain 10% *cis* isomer.

Isomerization of *cis*- to *trans*-β-Styryldiphenylarsine. A. Butyllithium.—A solution of approximately 0.5 g of *cis*-β-styryldiphenylarsine in 20 ml of THF was treated with 20 ml of a 15% solution of butyllithium in hexane at reflux for 2 hr. The mixture was allowed to stand under nitrogen for 24 hr and analyzed by vapor–liquid preparative chromatography at 200°. There was no *trans* isomer present.

B. Phosphorus Trichloride.—In a similar reaction, the *cis*-arsine was refluxed with 2 g of phosphorus trichloride in 200 ml of THF. No isomerization occurred as shown by gas chromatography.

C. Phosphorus Pentachloride.—To a solution of approximately 0.5 g of *cis*-β-styryldiphenylarsine in 20 ml of THF, approximately 0.1 g of phosphorus pentachloride was added. The solution was refluxed for 2 hr. Gas chromatographic analysis at 200° showed only the *trans* isomer to be present.

Attempted Addition of Lithium Diphenylarsenide to the Styrylarsines.—To 0.5 g (0.0015 mole) of *cis*-β-styryldiphenylarsine in 20 ml of THF was added 5 ml (0.005 mole) of lithium diphenylarsenide. This solution was allowed to stand for 24 hr. Gas chromatographic analysis of the crude reaction mixture showed only the *cis* isomer to be present. Evaporation of the solvent and extraction of the semisolid with basic water (5% KOH) gave a solid identical with starting material as shown by mixture melting point determinations. The proton nmr spectrum of a deuteriochloroform solution of the crude solid before recrystallization showed no methylene or methyne proton signals, which would have indicated the presence of small amounts of phenylethylenebis(diphenylarsine).

Registry No.—I, 1013-87-2; II, 13084-50-9; III, 13084-51-0.

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Rearrangements of a 2-Vinylaziridine

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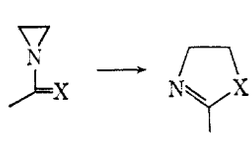
Aziridines possessing unsaturated substituents on nitrogen readily undergo ring expansion to 1-azacyclopentene derivatives.[1,2] Formally analogous to the



X = C<, O, S, N–

vinylcyclopropane–cyclopentene isomerization, these rearrangements have been effected by nucleophiles, acids, and heat. It was of interest to determine whether similar processes would occur in the 2-vinylaziridine system.

The model compound I was prepared by photolysis of the *p*-bromophenyl azide–isoprene adduct, a method that has been previously described.[3] On heating in xylene solution, I was converted in high yield to an isomeric compound (II). The infrared spectrum of the

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(2) H. W. Whitlock and G. L. Smith, *Tetrahedron Letters*, No. 19, 1389 (1965).
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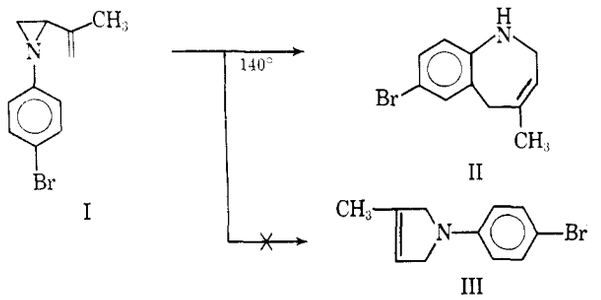
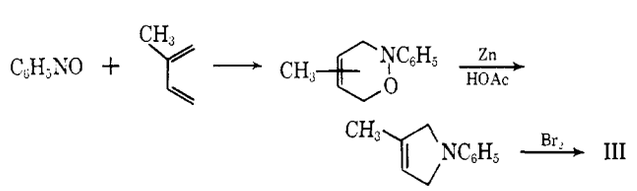


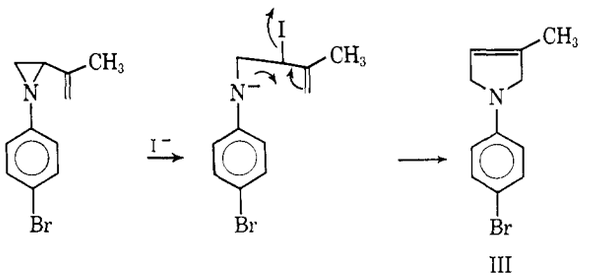
product displayed an NH absorption and treatment with phenyl isothiocyanate afforded a phenylthiourea derivative. The nmr spectrum of II showed three aromatic hydrogens, one vinyl hydrogen (τ 4.70, multiplet), and three methyl hydrogens (τ 8.22, doublet, J = 1.4 cps). A multiplet at τ 6.45 (2 H, α to N), a singlet at τ 6.70 (NH), and a singlet at τ 6.67 (2 H, benzylic) completed the spectrum. The chemical-shift assignment for the amino hydrogen was established by deuterium exchange. These data are consistent with the assigned structure (II), but cannot be reconciled with ring expansion to pyrroline III or its Δ^2 isomer. Furthermore, an authentic sample of III did not isomerize to II under the conditions of the experiment.

Rather than the anticipated isomerization to the pyrroline, aziridine I underwent the infrequently observed amino Claisen rearrangement.[4] In their analysis of the energetics of this reaction, Marcinkiewicz, *et al.*, have found that an activation energy at least 6 kcal/mole greater than that of corresponding oxygen Claisen rearrangement is required.[5] Thus, owing to the intervention of fragmentation reactions, pyrolysis of N-allylaniline gives aniline and propene instead of *o*-allylaniline.[6] A value of 12–14 kcal/mole has been cited for the strain energy associated with the aziridine ring.[7] It therefore seems probable that the observed amino Claisen rearrangement of I is made energetically feasible by the relief of aziridine ring strain in the transition state.

When I was treated with sodium iodide in refluxing acetone, it smoothly rearranged to 1-*p*-bromophenyl-3-methyl-3-pyrroline (III). The identity of the product was established by elemental analysis, spectral data, and independent synthesis.



As suggested by Heine for the rearrangement of N-aroylaziridines to Δ^2-oxazolines,[1] the reaction may be interpreted as involving nucleophilic attack of iodide on the aziridine, followed by displacement of iodide, in the manner indicated. In view of the present results, the alternative path proposed for N-aroyl-



aziridine-Δ^2-oxazoline isomerization (I^- attack on the carbonyl carbon)[1] appears somewhat less probable. Extension of the nucleophile-catalyzed ring-expansion reaction to the 2-vinylaziridine system provides a new entry into the five-membered heterocycle series.

Experimental Section[8]

1-*p*-Bromophenyl-2-isopropenylaziridine (I).—A solution of 9.9 g (0.05 mole) of *p*-bromophenyl azide and 25 ml of isoprene was refluxed for 13 days. Removal of one-half of the excess isoprene and cooling gave 7.1 g (54%) of white crystalline solid, mp 112–115°. Three recrystallizations from *n*-hexane gave the triazoline adduct, mp 115.0–115.5°.

Anal. Calcd for $C_{11}H_{12}BrN_3$: C, 49.64; H, 4.55; N, 15.79. Found: C, 49.64; H, 4.56; N, 15.79.

A solution of 2.4 g (9.0 mmoles) of the triazoline in 30 ml of benzene and 20 ml of acetone was irradiated (25°) in a Pyrex tube with a 450-w Hanovia Type L source for 10 hr. Removal of the solvent gave 2.3 g of oil that crystallized on standing, mp 33–37°. Four crystallizations from pentane (−78°) and sublimation at 40° (0.5 mm) gave pure I, mp 49.5–50.5°.

Anal. Calcd for $C_{11}H_{12}BrN$: C, 55.48; H, 5.08; N, 5.85. Found: C, 55.54; H, 5.27; N, 5.87.

The infrared spectrum showed no absorption in the C=N region (1690–1640 cm^{-1}). In addition to four aromatic hydrogens, the nmr showed two vinyl hydrogens (τ 4.87 and 4.73), a methyl group (doublet, τ 8.22, J = 1.0 cps), and three aziridine ring hydrogens (multiplet, τ 8.00–7.29).

Thermal Rearrangement. 7-Bromo-4-methyl-2,5-dihydro-1H-1-benzazepine (II).—A solution of freshly sublimed I, 1.9 g in 30 ml of anhydrous xylene, was purged with a stream of purified nitrogen and then refluxed under nitrogen for 17 hr. Removal of the solvent under reduced pressure gave 1.9 g of a pale yellow oil. Vapor phase chromatography (3-ft Carbowax 20 M, 250°) and infrared analysis showed that this material was about 95% II. The crude product distilled from 130 to 136° (1.2 mm); 1.4 g collected. Redistillation gave the analytical sample.

Anal. Calcd for $C_{11}H_{12}BrN$: C, 55.48; H, 5.08; Br, 33.56; N, 5.88. Found: C, 55.30; H, 5.28; Br, 33.40; N, 5.89.

A sample of II dissolved in ethanol was treated with picric acid, heated to boiling, and then cooled. The crystallized picrate derivative was collected and recrystallized from methanol, mp 175–176°.

Anal. Calcd for $C_{17}H_{15}BrN_4O_7$: C, 43.70; H, 3.24; Br, 17.10; N, 11.99. Found: C, 43.99; H, 3.38; Br, 17.07; N, 11.89.

A sample of II and phenyl isothiocyanate were heated over a low flame for 3 min. After cooling and dilution with *n*-hexane, the product was collected. Recrystallization from methanol gave material melting at 147–148°. The infrared and nmr (hexadeuterioacetone) spectra showed this compound to be the phenylthiourea derivative of II.

Iodide-Catalyzed Rearrangement. 1-*p*-Bromophenyl-3-methyl-3-pyrroline (III).—A solution containing 0.45 g of I, 2.3 g of sodium iodide, and 40 ml of acetone was refluxed for 41 hr. Removal of the solvent under reduced pressure gave a tan solid that was washed with three 10-ml portions of cold water: yield 0.41 g (91%), mp 98–108°. Recrystallization from methanol gave pure III (infrared, nmr, mixture melting point), mp 121–122°.

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1-*p*-Bromophenyl-3-methyl-3-pyrroline (III).—At 0°, a solution of 7.5 g (0.07 mole) of nitrosobenzene in 40 ml of benzene and 40 ml of ether was combined with 6.8 g (0.10 mole) of isoprene in 20 ml of ether. After 64 hr at 0°, the solvent was removed and the product (2-phenyl-4- and/or -5-methyl-3,6-dihydro-1,2-oxazine) distilled at 95–110° (1.4 mm) [lit.[9] bp 126–130° (12 mm], yield 5.3 g (43%). The product (5.3 g) in 20 ml of glacial acetic acid was treated (cooling) with 6.5 g of powdered zinc. After the initial exothermic reaction had moderated, the mixture was refluxed for 4 hr. A solution of 17 g of sodium hydroxide in 40 ml of water was added to the cooled mixture and the resulting suspension filtered. The residue was washed with three 40-ml portions of boiling benzene and the aqueous and organic layers (filtrate) were separated. Evaporation of the solvent gave 5 g of tan solid which afforded 1.4 g (29%) of 3-methyl-1-phenyl-3-pyrroline after recrystallization from methanol, mp 88–90° (lit.[9] mp 89–90°).

The pyrroline was brominated in carbon tetrachloride by the method of Roberts and Ross.[10] Three recrystallizations from methanol gave the analytical sample, mp 120–121°.

Anal. Calcd for $C_{11}H_{12}BrN$: C, 55.48; H, 5.08; N, 5.88. Found: C, 55.36; H, 4.92; N, 5.84.

Registry No.—I, 13116-35-3; II, 13124-63-5; II picrate derivative, 13124-64-6; III, 13119-23-8; triazaline adduct, 13124-65-7.

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2-(2′,6′-Dimethoxyphenyl)-1,3-dioxolenium Fluoroborate. A Stable Carboxonium Salt. Reactions as an Alkylating Agent[1]

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We have in the past studied arylations by diaryliodonium salts,[3] and a recent publication reports an ethynylation and vinylation by iodonium salts.[4] While alkyliodonium salts are presently unknown, stable oxonium salts are known; they first were reported by Meerwein and co-workers in 1937.[5] The most useful reaction to date of trialkyloxonium salts[6–9] is the facile alkylation of nucleophiles.[7–9] The very stable triphenyloxonium fluoroborate, first prepared by Nesmeyanov,[10] is reported to be an arylating agent.

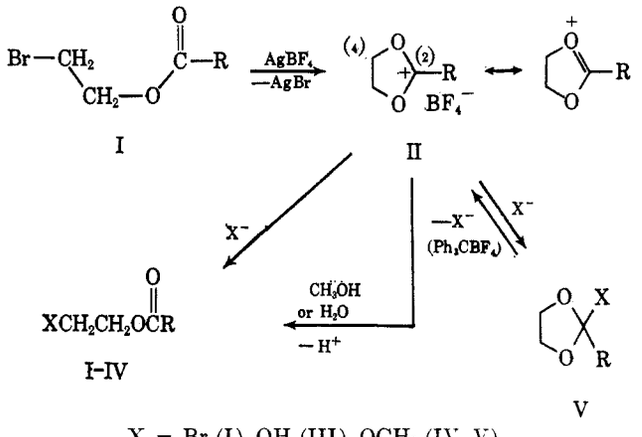
Numerous resonance-stabilized carboxonium salts have been prepared by Meerwein and co-workers[11,12] by alkylation of the carbonyl groups of aldehydes, ketones, esters, lactones, amides, and lactams with trialkyloxonium salts or with alkyl halides in the presence of silver fluoroborate.[7b,11]

The five-membered cyclic 1,3-dioxolenium ions have enhanced stability; indeed, some have been isolated as the hydrogen sulfates.[11] The 2-phenyl-1,3-dioxolenium fluoroborate has been prepared by Meerwein and co-workers,[11,12] who reported its reaction to be that of both carbonium and oxonium ions. Strong nucleophiles (CH_3O^-, CN^-) reacted at the 2 position without ring cleavage while others reacted with ring opening to give β-substituted ethyl esters.

It was our aim to prepare an even more stable 1,3-dioxolenium salt having the electron-releasing 2,6-dimethoxyphenyl substituent at the 2 position. It was believed that such stabilization of the cation would increase its selectivity toward nucleophiles, resulting in alkylation by displacement at the 4 position. It seemed likely that reaction at the 2 position would be reversible and rate controlled, while reaction of the 4 position would be irreversible and thermodynamically controlled. The preparation of such a salt is now reported as are its reactions as an alkylating agent toward carbon, nitrogen, oxygen, and sulfur atoms in nucleophilic molecules; several of these reactions are previously unreported.

The cyclization of β-bromoethyl 2,6-dimethoxybenzoate (I) in the presence of anhydrous silver fluoroborate in ether gave 2-(2′,6′-dimethoxyphenyl)-1,3-dioxolenium fluoroborate (II) (Scheme I); compounds I and II are previously unreported.

SCHEME I



X = Br (I), OH (III), OCH_3 (IV, V)
R = 2,6-dimethoxyphenyl (I–V)

We now report the first nmr spectrum of a dioxolenium salt, that of II in trifluoroacetic acid: a triplet centered around τ 2.27 for the *para* hydrogens, a doublet at 3.39 for the *meta* hydrogens (J = 8.6 cps), a singlet at 4.77 for the methylene protons of the five-membered ring, indicating strong deshielding by the positive charge, and a singlet at 6.06 for the methoxyl hydrogens. The ultraviolet spectra of carboxonium

(1) This research was supported by a fellowship from the National Cancer Institute, Public Health Service, National Institutes of Health, No. 1 F2 CA-19,690-02.
(2) National Institutes of Health Postdoctoral Fellow, 1963–1965.
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